Filter Media for Nutrient Removal in Natural Systems and Built Environments: I—Previous Trends and Perspectives

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Abstract

High nitrogen and phosphorus concentrations in stormwater runoff, contaminated groundwater, landfill leachate, and domestic and industrial wastewater effluents have aggravated groundwater and surface water contamination and hindered the potential of water reuse. Elevated nutrient levels in groundwater and surface water systems may cause public health problems and may impair or destroy environmentally sensitive eco-system habitats. Multiple pollutants with cotreatment strategies have not yet been fully developed. Design philosophy is evolving to fit versatile application needs with the most cost-effective way to ensure environmental compliance. These nutrients can actually be reduced or even removed to a large extent by using a filter or sorption media mixture throughout the applications of low-impact development and best management practices. The objective of this critical and thorough literature review was to provide a comprehensive realization of the use of sorption media mixtures for nutrient removal in a number of major environmental engineering disciplines. Classification of the disciplinary applications at a practical level provides some viewpoints of the trends and perspectives along this endeavor in the nexus of materials science, sustainable engineering, and green infrastructure.

Key words: sorption media; nutrient removal; environmental remediation; green materials; green engineering

Introduction

MUCH OF ENVIRONMENTAL MANAGEMENT in the past few decades focused on point-source pollution of industrial and municipal effluent. Not until very recent years, comparable effort was made to restrict the input of nitrogen (N) and phosphorus (P) from dispersed or nonpoint sources such as agricultural and urban runoff. Within these dispersed or nonpoint sources, stormwater runoff is just one possible source of nitrogen; others include septic tanks and land-based application of reclaimed wastewater or fertilizer, which can even elevate nitrate and nitrite concentrations in many aquifer systems. For example, although residents in towns and cities are served by centralized wastewater treatment facilities, >25 million homes, or 25% of the U.S. population, still use on-site wastewater treatment systems to meet their wastewater treatment and disposal needs (USEPA, 2003). To provide a more specific example, ~2.5 million on-site wastewater treatment systems are currently permitted in the State of Florida alone. Because of widespread septic tank failure, anthropogenic inputs of nonpoint pollutants, particularly N and

P, have accumulated dramatically in the groundwater aqui-fer. As a consequence, it has been shown that nitrate concentrations have increased in many Upper Floridian aquifer springs since the 1950s. Phelps (2004) reported that nitrate concentrations ranged from <0.02 to 12 mg/L, with a median of 1.2 mg/L, for 56 Upper Floridian aquifer wells sampled in Marion County during 2000–2001. Besides, nitrate concentrations have exceeded 10 mg/L in recent years at some springs in Lake, Marion, Orange, Seminole, and Volusia Counties, according to Phelps *et al.* (2006) and the St. Johns River Water Management District (SJRWMD, 2008). Increasing trends in nitrate concentration were documented in Volusia County springs, such as DeLeon and Gemini Springs (Phelps *et al.*, 2006) and Blue Spring (SJRWMD, 2008). Thus, violation of environmental compliance of the maximum contaminant level for nitrate in drinking water, which was set at 10 mg/L nitrate-nitrogen (NO_3-N) and 1 mg/L nitrite-nitrogen (NO_2-N) by USEPA (1988), became an acute environmental issue. Hence, how to sustain the quality of sources of potable water with respect to high nutrient concentrations has long been a challenge in environmental engineering.

Nutrient pollution is the common threat that links an array of problems from stormwater to groundwater, wastewater, and drinking water all over the world. These nutrient species have direct and indirect effects on human health and the aquatic ecosystem. To deal with this issue, environmental

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engineers oftentimes integrate physical, chemical, and biological treatment methods in a complex regulatory framework to control and remediate the corresponding pollution impacts. It is an emerging field that promotes water treatment efficiencies and effectiveness, creating a new dimension of material design and synthesis for green infrastructure in environmental engineering science. In fact, engineered, functionalized, and natural sorption media can be used to treat stormwater runoff, wastewater effluents, groundwater flows, landfill leachates, and sources of drinking water for nutrient removal via both physicochemical and microbiological processes. This approach for stormwater and wastewater treatment has "green" implications because of the inclusion of recycled materials as part of the material mixture, promoting treatment efficiencies and effectiveness. The improvement of such filter materials that may remove particular types of nutrient pollutants has not yet been fully studied, although some laboratory and field works have been completed.

Removal of ammonia, nitrite, nitrate, and phosphorus can be achieved collectively or independently using sawdust (Kim et al., 2000; Gan et al., 2004; Schipper et al., 2005), tire crumb (Shin et al., 1999; Lisi et al., 2004; Smith et al., 2008), sand (Harris et al., 1996; DeBusk et al., 1997; Clark et al., 2001; Birch et al., 2005; Forbes et al., 2005; Güngör and Ünlü, 2005; Hsieh and Davis, 2005; Seelsaen et al., 2006), clay (Gisvold et al., 2000; Gálvez et al., 2003), zeolite (Clark et al., 2001; Li, 2003; AEC, 2005; Birch et al., 2005; Seelsaen et al., 2006), sulfur (Zhang, 2002; Ray et al., 2006), limestone (Kim et al., 2000; Zhang, 2002; Sengupta and Ergas, 2006), etc., which are deemed as multifunctional materials applicable to natural systems and built environments, improving both physicochemical and microbiological processes.

The adsorption, absorption, ion exchange, and precipitation processes are actually intertwined with the overall physicochemical process when removing nutrient via socalled "green sorption media." Pollutants removed by the adsorption process in green sorption media may subsequently desorb. If there are organic sources in the environment, hydrolysis converts particulate organic N to soluble organic N, and ammonification in turn releases ammonia into the water bodies. Ammonia may be sorbed by clay in bioretention filters filled with sorption media. However, nitrate, which is quite soluble, may be sorbed first and then leached from the clay during subsequent storm events, rejuvenating the sorptive capacity for subsequently incoming nutrients. In addition to ammonification, important biochemical transformation processes include nitrification and denitrification. They result in the transformation of nitrogen between ammonia, nitrite, and nitrate forms via oxidation and reduction reactions in microbiological processes. Nitrification is a microbiologically mediated process that occurs under aerobic conditions, resulting in the formation of nitrate, whereas denitrification is also a microbiologically mediated process, but occurs under anaerobic (oxygen depleted) conditions, resulting in the formation of gaseous forms of nitrogen. In reduction–oxidation chemistry, nitrification is a process in which ammonium is oxidized and denitrification is a process in which nitrate is reduced. Denitrification also requires the presence of an electron donor, which may commonly include organic carbon, iron, manganese, or sulfur, to bring about the reduction. Without these electron donors, denitrification is infeasible even in anaerobic environments. Although these physicochemical and microbiological processes have been well studied, the following critical questions have not been fully answered in the literature: (1) What are the underlying integrated processes and their function, effectiveness, and longevity associated with different mixtures of sorption media? (2) How such systems are designed, installed, maintained, controlled, and replaced for various nutrient control goals? (3) What methods are available for the comparison of cost-effectiveness of the performance of green sorption media in engineering processes?

The objective of this thorough literature review was to provide a comprehensive realization of the use of sorption media mixtures for nutrient removal in a number of major environmental engineering disciplines (e.g., stormwater treatment, groundwater remediation, wastewater treatment, and drinking water treatment) (Harris et al., 1996; DeBusk et al., 1997; Kim et al., 2000; Clark et al., 2001; Gan et al., 2004; Birch et al., 2005; Forbes et al., 2005; Güngör and Ünlü, 2005; Hsieh and Davis, 2005; Schipper et al., 2005; Seelsaen et al., 2006). The removal efficiency of a variety of systems with different materials, design ideas, and associated environmental benefits are identified and summarized based on both functional and chronological aspects. Key media characteristics with application potentials are discussed based on the results with several selected recipes for the purpose of demonstration. This leads to examine some of the aforementioned key questions in regard to assessing an integration of the planning, design, siting, installation, maintenance, and management functions as a companion paper, to aid in future design work of green engineering infrastructure holistically.

Review of State-of-the-Art Environmental Technologies for Nutrient Removal

Agricultural and urban runoff contains pollutants including nutrients, sediment, animal wastes, salts, and pesticides. Many best management practices (BMPs) that have been proved effective can be used to control runoff and reduce the erosion and transport of sediment from urban settings and agricultural fields. For agricultural fields, these practices include conservation tillage, contour strip-cropping, terraces, filter strips, sediment retention ponds, and grade stabilization structures where sorption media may be deployed at strategic points to remove the nutrients. As for urban structural BMPs, such as infiltration devices, ponds, filters, and constructed wetlands, a variety of arrangements may be designed to accommodate various sorption media applications. Even nonstructural BMPs and low-impact development (LID) practices, such as rain gardens, bioswales, and permeable pavements, may be included for the applications of various sorption media.

Treating contaminated stormwater through either or both physicochemical or microbiological principles is an integral part of BMPs and LID when nutrient levels may be a major concern (Ray et al., 2006). Nutrients in stormwater can be removed by using physicochemical processes, such as activated carbon adsorption, ion exchange with synthetic resins, reverse osmosis, and electrodialysis. For example, phosphorus removal from stormwater may be achieved by both precipitation and adsorption processes. Some functionalized sorption media for phosphorus removal are sand rich in Fe, Ca, or magnesium (Mg); gravel; limestone (a sedimentary rock

largely composed of calcium carbonate [$CaCO_3$]); shale (fine grained sedimentary rock, mostly clay minerals); lightweight aggregates; zeolite (natural mineral or artificially produced alumino silicates); pelleted clay (along or in combination with soils); opaka (a siliceous sedimentary rock); pumice (a volcanic rock and natural porous mineral); wollastonite (a mineral containing calcium and ferrous metasilicate); fly ash (a residue generated from the combustion of coal); blast furnace slag (BFS—a porous nonmetallic coproduct in the iron and steel industry); alum (a hydrated aluminum potassium sulfate); goethite (a hydrous ferric oxide); hematite (a mineral form of iron(III) oxide [Fe_2O_3]); dolomite (a sedimentary carbonate rock or mineral composed of calcium magnesium carbonate [$CaMg(CO_3)_2$]); and calcite (a carbonate mineral) (Korkusuz et al., 2007). Mixtures of these materials as an integral part of the green sorption media would be very promising. Yet the leaching property of those materials is also of critical concern in environmental management.

Bioinfiltration, which is becoming one of the most frequently used stormwater management tools in urbanized watersheds, may be designed to facilitate microbiological processes with different filter media. These BMPs would be cost-effective when distributed over a site and incorporated into the stormwater collection system as part of the cornerstone of LID designs such as rain garden, bioinfiltration swales, bioinfiltration pond, and infiltration traffic island. Within the context of bioinfiltration, two important processes that result in the transformation of ammonia to nitrogen gas are nitrification by autotrophic bacteria and denitrification by either autotrophic or heterotrophic bacteria. For denitrification to occur, there is a need to ensure (1) the presence of nitrate and nitrite, which are the final products of nitrification and serve as the electron acceptor in denitrification, (2) the absence of dissolved oxygen (DO), (3) a facultative bacterial mass to use nitrate instead of oxygen as the electron acceptor, and (4) the presence of a suitable electron donor, such as the carbonaceous energy source for denitrification, which can either be internal (e.g., sawdust in sorption media, organic material present in wastewater) or external (methanol added to the treatment stage of denitrification).

Filter media can act as a harmless internal carbon source and supporting element for microbial colony development in any of the above BMPs and LID designs. However, additional treatment of the effluent may be required for those chemicals. The ultimate removal of N and P can be considered as part of the natural N and P cycles. Instead of relying on sorption media, however, some biological nutrient reduction wastewater treatment processes embedded in wastewater treatment plants are intended to remove nutrients by the following similar principles: mainly (1) the five-stage Bardenpho biological wastewater treatment system, which was developed for removing carbon, nitrogen, and phosphorus simultaneously; and (2) the anaerobic ammonia oxidation (ANAMMOX) process. The former is a biological heterotrophic process, whereas the latter is a biological autotrophic process in which ammonia is converted to nitrogen gas in the presence of nitrite under anoxic conditions using special microbes. In ANAMMOX, nitrite acts as an electron acceptor and no external carbon source is needed for denitrification as the bacteria are autotrophs (WEF et al., 2005). The ANAMMOX process is known to be active at temperatures between $6°C$ and $43°C$ and in the pH range of 6.7–8.3 (optimum is 8) (WEF

et al., 2005). Under optimum conditions, the maximum specific ammonium consumption rate is $99.00\,mg\ NH_4^+/g$ protein/min (WEF et al., 2005).

Phosphorus can also be removed by phosphorus-accumulating organisms in a biological treatment process with an aerobic stage. These phosphorus-accumulating organisms can accumulate an excess of phosphorus as polyphosphates in their cells. The system performance is generally good at a DO concentration of $\sim1.0\,mg/L$ and at pH >6.5. The system should have enough Mg, Ca, and K. Generally, municipal wastewaters have enough cations such as these. A system designed for nitrification cannot support biological phosphorus removal because of the presence of nitrate in the system. Hence, a denitrification system should be included in a separate chamber when biological phosphorus removal is an issue. In an anaerobic stage, the stored phosphorus is generally released (WEF et al., 2005).

Although nitrification and denitrification are popular for stormwater and wastewater treatments, they are also being used for drinking water treatment in Europe and elsewhere. Riverbank filtration (RBF) is an environmentally sustainable and cost-effective water treatment technology, which has been used for centuries to remove pollutants and microorganisms from surface water (Tufenkji et al., 2002). The hydraulic and hydrochemical processes of the RBF technique also follow essential physicochemical and microbiological principles. Understanding the mass balance of the catchment area based on transient river stages and recharge, geological factors, and spatial changes in the water chemistry is required to determine the quantity of bank filtrate that could be in the nexus of the sorption media. Groundwater and landfill leachate treatment processes are similar to stormwater and wastewater treatment processes, respectively.

In regard to nitrogen removal, the higher surface area of clay in natural soil might be able to provide more contact area for the solid to absorb and more space for the bacterial colony to develop. Most filter media may improve solid–liquid contact with higher surface area, prevent channeling with a better particle distribution, and provide a better ion exchange capacity to support absorption/adsorption, a better retaining capability for adsorbed nutrient, and more surface area for the bacterial colony to develop. Thus, filter media can support both physical and biological processes simultaneously. In regard to phosphorus removal, a number of different technologies are applicable, including (1) chemical precipitation, (2) biological treatment, (3) crystallization, (4) ion exchange, (5) magnetic separation, (6) adsorption/absorption, (7) tertiary filtration, and (8) sludge treatment (Lazaridis, 2003). A combination of differing technologies is critical for promoting collective removal of several pollutants.

Nitrogen and phosphorus species present in the aforementioned processes can appear in different forms in water bodies. The different nutrient forms are defined and summarized in Appendix.

Stormwater treatment by sorption media

Before 1995, much work tried to remove nutrients primarily with the sand filter method. For this reason, three main types of sand filters were developed: (1) the Washington D.C. sand filter method, (2) the Delaware sand filter design, and (3) the Austin sand filter (USEPA, 1999). The removal efficiency

of the Delaware sand filter is solids 70.2%, total phosphorus (TP) 71.1%, NH_3-N 6.7%, and total Kjeldahl nitrogen (TKN) 59.9% (Bell et al., 1995). These filter methods gave promising results but could not remove all nutrients. Faced with this situation, some researchers began investigating new concepts to remove all nutrient species. Sorption media were found to be a very good means for nutrient removal from water bodies. Table 1 summarizes the use of sorption media to treat stormwater.

Richman (1997) found that compost had good removal of 90% solids, 85% oil and greases (O/G), and 82%–98% heavy metals by adsorption. DeBusk et al. (1997) used sand (with quartz), fresh organic (peat) soil, crushed lime rock (2.50 cm nominal size), and wollastonite to remove TP, copper (Cu), nickel (Ni), and cadmium (Cd) from stormwater. They found that wallastonite (essentially calcium inosilicate [$CaSiO_3$]) had very good removal efficiency for their targeted contaminants. Wallastonite could remove about 87.8% P, 97.7% Cd, 81.4% Cu, and 80.3% Ni by adsorption. On the other hand, limerock, peat, and sand could remove 41.4%, 44%, and 41.4% of P, respectively, in the stormwater runoff. It was concluded that wallastonite is very effective in phosphorus removal because it contains calcium and ferrous ions (Debusk et al., 1997). Calcium and ferrous ions can remove phosphorus by precipitation or adsorption.

Kim et al. (2000) used different kinds of filter media, such as alfalfa, leaf mulch compost, newspaper, sawdust, wheat straw, and wood chips, for biological removal of nitrate from stormwater runoff. Alfalfa, newspaper, and compost were grouped in one experiment and sawdust, wheat straw, and wood chips were in the other. The particle size of the media is shown in Table 1. A total of eight columns (40 cm long, 6.4 cm inner diameter) were used. Among them, two columns were used as controls, using only washed silica sand. All columns were operated at a temperature of $22°C \pm 2°C$. The columns were seeded by secondary effluent sample and those seeded materials were run for 2 days. The authors found that alfalfa and newspaper had 100% nitrate removal efficiency, but mulch compost had only 60%. They also found that sawdust, wheat straw, and wood chips had good removal efficiency (>95%), but wood chips showed consistently better performance than sawdust for nitrate removal. It was concluded that all of these were electron donors and good carbon sources for promoting denitrification. They suggested that increasing the hydraulic retention time (HRT) may result in better removal. They also found that soil could only remove 7%–10% of nitrate because of its anionic form (Kim et al., 2000). Nitrate removal is performed by other processes in combination with biological processes. If only the biological processes were occurring, different media should provide different removal efficiencies. This might be a combined effect of adsorption and biological process.

Clark et al. (2001) conducted experiments to improve the quality of stormwater runoff by using activated carbon, peat moss, compost, and sand in aerobic and anaerobic conditions. They suggested that sorption media might not be capable of retaining the sorbed materials under anaerobic conditions (Clark et al., 2001). There might be several reasons such as pH of the system, bonding between solids and adsorbed materials, and competition between ions present in the liquid phase for desorption, which can be influenced by the retention time and amount of media. If desorption only occurs under the anaerobic condition, there should not be any leachate from landfills. Tufenkji et al. (2002) used the RBF method to remove pathogenic microbes from surface water. The RBF method is also very effective for the removal of natural organic matter (OM—dissolved and particulate humic and nonhumic organic substances), odorous compounds (e.g., geosmin), fragrance compounds (e.g., menthol, limonene, and α-terpineol), and aromatic hydrocarbons. The RBF removes the pollutants by sorption, precipitation, redox reactions, complexation with OM, microbial degradation, and dilution. The success of RBF depends on raw water quality, characteristics of the bed sediments, and retention time. So each site should be considered separately, and success at one site will not always indicate that it will be helpful for other sites. It is also mentioned that the EPA is emphasizing bank filtration for the removal of Cryptosporidium. The Cryptosporidium oocysts (4–6 μm) and Giardia cysts (9–12 μm) can be removed by interception (i.e., the microbes will encounter a collector grain because of its size and moving path) and gravitational sedimentation (i.e., the microbes will settle on a collector grain because of gravitational force) (Tufenkji et al., 2002). The effectiveness of RBF for nutrient removal was not assessed. If the surrounding soil has clay with mineral content, it should be an effective process for phosphorus removal. Soil can also support the growth of nitrifiers and so it should also be effective for the removal of ammonium and nitrite. But it may not work for nitrate removal as it is known that soil particles have little affinity for nitrate. The RBF process and sorption media can be used together. In a bank filtration, filter media can be placed around the well to help to remove nutrients. Tshabalala (2002) also tried to remove pesticides with lignocellulosic materials as the media, which removed about 82% of dichlobenil, 92% of chlorothalonil, and 96% of chlorpyrifos by adsorption.

Boving and Zhang (2004) used aspen wood (Populus tremula) fibers to remove aqueous phase polynuclear aromatic hydrocarbons (PAH) such as naphthalene (NP), pyrene, anthracene, and fluorene from stormwater runoff in a column study. The ultimate removal of anthracene was 60%, pyrene was 89%, and fluorene was 36%. NP was poorly attracted by the wood fibers. The results implied that the sorption of PAH by aspen wood was related to the hydrophobicity and molecular weight of PAH. The authors also observed some desorption phenomena, but desorption was slower than adsorption. The sorption rate slowed over time and smaller particles had a greater sorption capability. Hsieh and Davis (2005) carried out experiments on urban stormwater runoff in 18 columns filled with different media mixtures composed of mulch, soil, and sand. Mulch was very effective at removing nitrate, much more than sand (i.e., about 43% of nitrate was removed by a mulch and sand mixture, but sand alone could remove about 11% nitrate). However, mulch could not remove ammonium or TP (only 4% TP removed), the reasons for which were not explained by the authors. For all media mixtures tested, ammonium removal was between 2% and 26% and nitrate removal was 1%–43%. They concluded that soils with higher silt/clay contents, higher cation (Mg/Ca/K) contents, more OM, and greater cation exchange capacity might be very effective in nutrient removal and that coarse media might not be able to retain the nutrient in repetitive loading because of the small surface area available. Good TP removal ($\sim$41%–48%) was observed by three types of sandy

TABLE 1. SORPTION MEDIA USED TO TREAT STORMWATER

No.	Sorption media	Additional environmental benefits	Physical/chemical properties	References
1	Sandy coastal soil			Harris et al. (1996)
2	Compost	O/G, heavy metals	Maple and elm leaf compost	Richman (1997)
3	Peat Wollastonite Limerock Sand with quartz	Cu, Cd, Ni		DeBusk et al. (1997)
4	Alfalfa Leaf mulch compost Sawdust Wheat straw Wood chips Newspaper Sulfur Limestone		$D < 4\,mm$ $D < 2\,mm$ $D < 2\,mm$ $D < 4\,mm$ $D < 2\,mm$ D (average) $< 4\,mm$ Large particles 2–2.36 mm and small particles 0.6–1.18 mm $D = 0.6$–1.18 mm	Kim et al. (2000)
5	Crushed piping materials	Organics		Li et al. (2000)
6	Iron sulfide			Tesoriero et al. (2000)
7	Peat Carbon sand, enretech sand, or sand Zeolites Activated carbon	Cu, Fe, Pb, Zn		Clark et al. (2001)
8	Natural sand (bank filtration)			Tufenkji et al. (2002)
9	Wood fibers	Polynuclear aromatic hydrocarbons	Aspen wood fibers composed of 51% cellulose, 26% hemicellulose, 21% lignin, and 1% ash	Boving and Zhang (2004)
10	Lignocellulosic material		Basically pine bark chips	Tshabalala (2002)
11	Clay	Cd, Pb, Ni		Lazaridis (2003)
12	Zeolites			Birch et al. (2005)
13	Opoka	Microorganisms		Braun-Howland (2003)
14	Waste medium density fiberboard sawdust			Gan et al. (2004)
15	Mulch Soil Sand	Lead, TSS, O/G	SL Sand	Hsieh and Davis (2005)
16	Zeolites Pure quartzitic sand	Cu, Pb, Zn		Birch et al. (2005)
17	Allophane Chitin Pumice Bentonite Steel slag Lime stone Zeolites		Iron (18.2%), aluminum (13.7%), calcium (12.7%), magnesium (7.3%), and other 4%–8% $CaCO_3$	AEC (2005)
18	Hard wood Mulch	Cu, Cd, Cr, Zn, Pb, DCB, NP, FA, BP	Silver maple, Norway maple, red oak, and cherry mulch; size 4,760 μm	Ray et al. (2006)
19	Wood fibers Sand Zeolites Glass Ash Compost	Zn, Cu	$D = 4\,mm$ $D = 4\,mm$	Seelsaen et al. (2006)
20	Iron sulfide			Baeseman et al. (2006)
21	Metallic iron Clinoptilolite	Fe	$D = 0.006$–0.01 mm; surface area 0.31 m²/g $D = 0.18$–4 mm	Huang et al. (2006)

BP, benzopyrene; D, diameter of the media; DCB, dichlorobenzene; FA, fluoranthene; NP, naphthalene; O/G, oil and grease; SL, sandy loam; TSS, total suspended solids.

TABLE 2. NUTRIENT REMOVAL EFFICIENCY OF DIFFERENT SORPTION MEDIA IN STORMWATER TREATMENT

No.	Sorption media	Mechanism	Removal efficiency	References
1	Compost	Adsorption	90% solids, 85% oils and greases, and 82%–98% heavy metals	Richman (1997)
2	Wollastonite	Adsorption	87.8% TP (initial concentration 0.40 mg P/L, for all cases), 81.4% Cu (initial concentration 0.03 mg/L, for all cases), 97.7% Cd (initial concentration 0.015 mg/L, for all cases), and 80.3% Ni (initial concentration 0.015 mg/L, for all cases)	DeBusk et al. (1997)
	Limerock		41.5% TP, 32.2% Cu, 81.34% Cd, and 31.3% Ni	
	Peat		44.% TP, 41.2% Cu, 97.8% Cd, and 92.3% Ni	
	Sand		41.50% TP, 76.95% Cu, 94.40% Cd, and 77.67% Ni	
3	Sulfur	Nitrification/ denitrification	Not reported	Kim et al. (2000)
	Alfalfa		100% nitrate (initial concentration 2.00 mg N/L)	
	Leaf mulch compost		60% nitrate (initial concentration 2.00 mg N/L)	
	Newspaper		100% nitrate (initial concentration 2.0 mg N/L)	
	Sawdust		>95% nitrate (initial concentration 2.00 mg N/L)	
	Wheat straw		>95% nitrate (initial concentration 2.00 mg N/L)	
	Wood chips		>95% nitrate (initial concentration 2.00 mg N/L)	
4	Lignocellulosic materials	Adsorption	82% dichlobenil (initial concentration 0.04 mg/L, for all cases) 92% chlorothalonil 96% chlorpyrifos	Tshabalala (2002)
5	Aspen wood fibers	Adsorption	60% anthracene (initial concentration 0.05 mg/L) 89% pyrene (initial concentration 0.05 mg/L) 36% fluorine (initial concentration 0.05 mg/L)	Boving and Zhang (2004)
6	100% sand	Adsorption	96% TSS, 96% O/G, 98% lead, 85% TP, 11% nitrate, and 8% ammonia (initial phosphorus concentration 3 mg P/L, nitrate concentration 2 mg N/L, ammonium concentration 2 mg N/L, motor oil 20 mg/L, for all cases)	Hsieh and Davis (2005)
	100% sand		96% TSS, 96% O/G, 96% lead, 10% TP, 1% nitrate, and 15% ammonia	
	2% mulch, 93% soil, 5% sand		29% TSS, 96% O/G, 98% lead, 47% TP, 1% nitrate, and 6% ammonia	
	2% mulch, 93% soil, 5% sand		88% TSS, 96% O/G, 98% lead, 41% TP, 14% nitrate, and 24% ammonia	
	2% mulch, 93% soil, 5.00% sand		91% TSS, 96% O/G, 98% lead, 48% TP, 8% nitrate, and 16% ammonia	
	91% mulch, 9% sand		86% TSS, 96% O/G, 75% lead, 4% TP, 43% nitrate, and 16% ammonia	
	100% sand		96% O/G, 66% lead, 84% TP, 13% nitrate, and 5% ammonia	
	3% mulch, 97% sand		96% TSS, 96% O/G, 98% lead, 61% TP, 9% nitrate, and 9% ammonia	

	Material	Method	Results	Reference
	2% mulch, 21% soil, 77% sand		66% TSS, 96% O/G, 98% lead, 47% TP, 3% nitrate, and 2% ammonia	
	8% mulch, 26% soil, 66% sand		94% TSS, 96% O/G, 98% lead, 50% TP, 4% nitrate, and 7% ammonia	
	6% mulch, 32% soil, 62% sand		93% TSS, 96% O/G, 98% lead, 39% TP, 4% nitrate, and 7% ammonia	
	24% soil, 76% sand		93% TSS, 96% O/G, 98% lead, 39% TP, 2% nitrate, and 5% ammonia	
	3% mulch, 43% soil, 54% sand		96% TSS, 96% O/G, 98% lead, 83% TP, 13% nitrate, and 26% ammonia	
	3% mulch, 24% soil, 73% sand		96% TSS, 96% O/G, 98% lead, 57% TP, 24% nitrate, and 17% ammonia	
	11% mulch, 19% soil, 70% sand		96% TSS, 96% O/G, 98% lead, 54% TP, 27% nitrate, and 20% ammonia	
	2% mulch, 17% soil, 81% sand		96% TSS, 96% O/G, 97% lead, 24% TP, 6% nitrate, and 11% ammonia	
	2% mulch, 72% soil, 26% sand		92% TSS, 96% O/G, 98% lead, 72% TP, 9% nitrate, and 19% ammonia	
	2.% mulch, 49% soil, 49% sand		92% TSS, 96% O/G, 98% lead, 71% TP, 9% nitrate, and 19% ammonia	Birch et al. (2005)
7	1:6 mixture of zeolite (having clinoptilolite) and coarse, pure quartzitic sand	Adsorption	47%–74% total Kjeldahl nitrogen (initial concentration 0.54–1.690 mg/L), 33%–40% TN (initial concentration 2.94–2.45 mg/L), 37%–67% TP (initial concentration 0.27–0.2 mg/L), 49%–81% Cu (initial concentration 0.013–0.019 mg/L), 88%–98% Pb (initial concentration 0.03–0.029 mg/L), −1%–77% Zn (initial concentration 0.19–0.39 mg/L), 10% Cr (initial concentration 0.0037 mg/L), −213%–38% Fe (initial concentration 0.15–2.16 mg/L), 20%–88% TSS (initial concentration 25–17 mg/L)	
8	Hardwood mulch	Adsorption (2 h HRT)	85% Cu, 75% Cd, 21% Cr, 90% Pb, 60% Zn, 63% DCB, 89% NP, FA, 90% BBP, 80% BP (initial concentration: Cu 0.992 mg/L, Cd 1,016 mg/L, Cr 0.989 mg/L, Pb 0.996 mg/L, Zn 1.079 mg/L, DCB 0.047 mg/L, NP 0.375 mg/L, FA 0.418 mg/L, BBP 0.4 mg/L, BP 0.815 mg/L)	
		Adsorption (4 h HRT)	85% Cu, 83% Cd, 26% Cr, 85% Pb, 72% Zn, 71% DCB, 65% NP, 95% FA, 95% BBP, 84% BP	
		Adsorption (72 h HRT)	85% Cu, 86% Cd, 68% Cr, 92% Pb, 72% Zn, 100% DCB, 88% NP, 93% FA, 77% BBP, 92% BP	Ray et al. (2006)
9	Fine glass	Adsorption	68% Zn (initial concentration 27 mg/L, for all cases) and 40% Cu (initial concentration 5 mg/L, for all cases)	
	Sand		15% Zn and 30% Cu	
	Course glass		15% Zn and 28% Cu	
	Ash		50% Zn and 97% Cu	
	Zeolite		97% Zn and 50% Cu	
	Compost		97% Zn and 90% Cu	
	Packing wood		88% Zn and 84% Cu	Seelsaen et al. (2006)
10	Clinoptilolite	Ion exchange	100% Fe	Huang et al. (2006)

BBP, butybenzylphthalate; HRT, hydraulic retention time; TN, total nitrogen; TP, total phosphorus.

loam soils; this was interpreted as caused by simple adsorption or complex sorption/precipitation processes (Arias et al., 2001; Hsieh and Davis, 2005). All three of these soils had significant fractions of sand (i.e., 66%–79%), clay (i.e., 12%–19%), and silt (i.e., 9%–15%). Across all media, TP removal was highly variable (i.e., from 4% to 85%), which might be related to properties of the sorption media used and the flow pattern of nutrient-laden water. As with the nitrogen contaminants, OM enhanced TP removal (about 93% TP removal) and a good correlation between OM and TP removal was established. They also tried to remove other chemicals such as O/G, Pb, and total suspended solids with sand, which provided >96% removal of all targeted compounds. Different mixtures of mulch, soil, and sand were also used to remove those compounds, all achieving noticeable removal. The authors suggested that total suspended solid removal at the upper layer or first stage of a bioretention system is very important to protect the system from clogging. They also conducted an on-site evaluation of rainfall events. About >99% O/G, >94% Pb, 31% NO_3-N, and >44% NH_4-N were removed by the process (Hsieh and Davis, 2005). The low removal of nitrogen compounds suggests that either mulch impedes the growth of nitrifiers or it cannot adsorb ammonium.

Birch et al. (2005) experimented with removing nitrogen species with a stormwater filtration basin (SIB) and flow through a filtration medium with a 1:6 mixture of zeolite (with clinoptilolite) and coarse, pure quartzitic sand. Their analysis revealed the valuable removal capabilities of SIB. TKN removal was about 47%–74% and total nitrogen (TN) removal was about 33%–40% (also some negative removal was observed). They found negative removal of NO_2^- and NO_3^- by the system. Sand was not effective in removing nitrate + nitrite and the denitrification capacity was not enough to support the removal system. On the other hand, nitrifiers may have been converting ammonia into nitrate so efficiently that the ultimate nitrate concentration in the effluent was increased, concealing the effects of the denitrifiers. TP removal was about 37%–67% by SIB. Clinoptilolite has an affinity for ammonium and it removes TN and TKN in an ion exchange process. Therefore, biological processes were not solely responsible for TN and TKN removal in this study. Clinoptilolite may be acting as an inhibitor of denitrifiers by promoting a less anaerobic condition. The pH of stormwater should be > 7 for the best removal of metals by the sorption media, otherwise the adsorbed metal ions will be quickly released.

Analytical and Environmental Consultants (AEC, 2005) investigated locally available adsorption materials to remove nutrient from surface and ground water. The materials tested were (1) allophane (an amorphous hydrous aluminum silicate clay mineral with an affinity for NH_4^+, NO_3^-, and PO_4^{3-}), which has a density of 2,000–2,200 kg/m^3 and surface area of 400–900 m^2/g; (2) bentonite (an impure clay, mostly montmorillonite, with an affinity for PO_4^{3-}), which has a density of 2,000–3,000 kg/m^3 and cation exchange capabilities of 70–100 meq/100 g; (3) chitin (a long-chain polymer and a derivative of glucose with an affinity for NH_4^+); (4) pumice (has an affinity for NO_3^- and PO_4^{3-}), which has a density of 600–800 kg/m^3 and cation exchange capabilities of 5–8 meq/100 g; (5) zeolite (with an affinity for NH_4^+, NO_3^-, and PO_4^{3-}), which has a density of about 1,700–2,100 kg/m^3, surface area of 145 m^2/g, and cation exchange capabilities of 80–200 meq/

100 g; (6) steel slag (has affinity for PO_4^{3-}); and (7) limestone. After their investigation factoring in local availability, cost, nutrient removal capability, environmental impact, and applicability, they identified allophane, zeolite, bentonite, steel slag, and limestone as the most suitable choices (AEC, 2005). These minerals can remove nutrients in an ion exchange and adsorption process.

Ray et al. (2006) used hardwood mulch to remove some metals (Cu, Cd, Cr, Pb, and Zn) and organics (dichlorobenzene, NP, fluoranthene, butybenzylphthalate, and benzopyrene) from urban stormwater runoff. These researchers suggested that (1) sorption capacity might be correlated with the ionic radii and molecular weight of the metal and organic contaminants, and (2) sorption by mulch varied with the concentration and species of contaminants (Ray et al., 2006). This experiment proved that sorption media are also very effective in metal removal. However, metal removal is affected by pH: (1) metal ions will be dispersed in solution under acidic pH and (2) ions will engage in precipitation reactions or adsorption under alkaline pH. Metal removal will be completely via an adsorption or ion exchange process because there is little possibility that metals will be removed by biological processes.

Seelsaen et al. (2006) used fine glass, sand, coarse glass, ash, zeolite, compost, and packing wood to remove heavy metals from stormwater. Huang et al. (2006) performed an experiment to remove nitrate with metallic iron, and ammonium ($NH_4^+ + NH_3$) and ferrous ions [Fe(II)] with clinoptilolite. They reported that acidic pH (i.e., $2.0 < pH < 4.5$) was an important factor for the removal of nitrate by Fe^0, which was very active at removing nitrate within a short time (i.e., about 30 min) in these conditions. The pH value and nitrate removal were inversely related. Nitrate removal was also inversely related to nitrate loading. It showed that when the nitrate loading was higher, there were insufficient iron surface sites to attract more nitrates, and ultimately, the removal efficiency was hampered. They also observed the appearance of ammonium when the nitrate was reducing in the redox sense. The removal of ammonium and Fe(II) by clinoptilolite was observed to depend on both pH and the F/N ratio (i.e., Fe(II) to $[NH_4^+] + [NH_3]$). Nitrate has a tendency to produce ammonium in the presence of Fe, which can be removed by clinoptilolite. Cliniptilolite is already well known for its ammonium removal capability, but it is too costly to use as a sorption media in a small-scale facility.

The preceding discussion was presented in chronological order to provide an overall picture of recent advancements in mixed media water treatment. Table 2 further summarizes the general success of the sorption media mentioned for removing various pollutants, especially nutrients, in the stormwater runoff under specified conditions.

Wastewater treatment by sorption media

Nutrient removal from wastewater is accomplished through adsorption and biological processes. The filter medium acts as a growth chamber for the microorganisms that are inoculated in the reactors. However, the removal of nutrient may not be accelerated by these dual effects. As the microorganisms are attached to the surface of the media, they reduce the surface area available for adsorption. Adsorption may be suppressed by biological processes in a sorption

media system if too much bacteria grow there. Thus, the growth of microorganisms has competing effects on water treatment by the system. Table 3 summarizes the sorption media that have been applied to wastewater treatment.

Shin et al. (1999) found that tire chips could adsorb volatile organic carbon from wastewater by a biological process and proved that it would be a good filter media (Shin et al., 1999). Han et al. (2001) used polyurethane-based porous media in an up-flow (UF) biological aerated filter (BAF) to treat wastewater at 18°C–22°C. The BAF consisted of a sludge drain, wastewater and air inlets, sampling ports, and effluent outlet. The porous media (about 70% of the reactor volume was filled) was used for the growth of autotrophic nitrifiers and denitrifiers. The nitrification reached nearly 100% and significant nitrogen loss was observed from the BAF. The heterotrophic denitrifiers were not responsible for this loss because there was no total organic carbon available in the system that could serve as electron donors. Nitrosomonas were

capable of denitrification using hydrogen and ammonium as electron donors in the absence of oxygen, but this process was very slow and could not solely account for the denitrification in the BAF. The authors ultimately concluded that the denitrification was completed by autotrophic nitrifiers and the ANAMMOX reaction in an anaerobic zone (Han et al., 2001). The maintenance of this kind of system and the growth of the ANAMMOX bacteria were critical.

Zhang (2002) performed an experiment to remove nitrate from wastewater by sulfur in a limestone autotrophic denitrification pond reactor. He assessed the effects of three variables on nitrate removal: (1) aerobic (mixed) and anoxic (unmixed) conditions, (2) the effect of temperature, and (3) the influence of chemical oxygen demand (COD)/N ratios in the feed. All the reactors contained sediment from a rural cattle pond and the sulfur and limestone were not covered by sediment. There were four types of reactors: (1) a reactor containing granular sulfur and limestone on sediment, (2) same

TABLE 3. SORPTION MEDIA USED TO TREAT WASTEWATER

No.	Sorption media	Additional environmental benefits	Physical/chemical properties	References
1	Sand filter			Bell et al. (1995)
2	Tire crumb/tire chips	2,4-dichlorophenol, 4-chlorophenol	$D = 20–40$ mm, surface area $403\,m^2/m^3$	Shin et al. (1999)
3	Zeolite + expanded clay		$D = 2.5–5$ mm	Gisvold et al. (2000)
4	Polyurethane porous media		Porous structure, average diameter 3–5 mm, external pore diameter $300\,\mu m$	Han et al. (2001)
5	Limestone		$D = 2.38–4.76$ mm	Zhang (2002)
	Sulfur		$D = 2.38–4.76$ mm	
6	Sand granules			Espino-Valdés et al. (2003)
7	Clay		Porosity 0.56	Gálvez et al. (2003)
8	High-density module			Rodgers and Zhan (2004)
9	SCL		Sand (53.28%), silt (24.0%), clay (22.72%)	Güngör and Ünlü (2005)
	LS		Sand (78.28%), silt (10.64%), clay (11.08%)	
	SL		Sand (70.28%), silt (14.64%), clay (15.08%)	
10	Masonry sand		Bulk density of masonry sand is $1,670\,kg/m^3$; porosity of masonry sand is 0.3	Forbes et al. (2005)
	Expanded shale		Expanded shale (SiO_2 62.06%, Al_2O_3 15.86%, Fe_2O_3 5.8%, CaO 1.44%, MgO 1.68%); bulk density of expanded shale is $728\,kg/m^3$; porosity of expanded shale is 0.59	
11	OSP		Powder form, 28% calcium, average particle size $200\,\mu m$, surface area $237\,m^2/g$	Namasivayam et al. (2005)
12	Limestone		$D = 2.38–4.76$ mm	Sengupta and Ergas (2006)
	Oyster shell			
	Marble chips		$Mg(OH)_2$ and $CaCO_3$	
13	Soy meal hull	Direct and acid dye	$D < 0.125$ mm	Arami et al. (2006)
14	Clinoptilolite			Hedström (2006)
	Blast furnace slag		Composed of melilite, merwinite, anorthite, and gehlenite	
15	Perlite			Joseph and Rodier (1995)
16	Clinoptilolite		$D = 0.30–4.76$ mm, density $0.88\,g/cm^3$	Smith et al. (2008)
	Expanded clay		$D = 0.40–5$ mm, density $0.656\,g/cm^3$	
	Tire crumb		$D = 0.30–5$ mm, density $0.4\,g/cm^3$	
	Sulfur		$D = 2.00–5$ mm, density $1.23\,g/cm^3$	
	Crushed oyster shell		$D = 3–15$ mm, density $1.31\,g/cm^3$	
	Utelite (expanded shale)		$D = 0.4–4.5$ mm, density $0.864\,g/cm^3$	

LS, loamy sand; OSP, oyster shell powder; SCL, sandy clay loam.

as reactor 1 but seeded with sulfur-based autotrophic deni-
trifers (i.e., *Thiobacillus denitrificans*), (3) a control case with
only the sediment, and (4) same as reactor 1 but with 1/3 less
sulfur and limestone by volume. He observed that the nitrate
removal was about 90%–100% with alkalinity control and
mixing and about 80%–85% without it; the control case had
very low but highly variable nitrate removal. Reactor 2 was
not used for testing the influence of temperature. Nitrate re-
moval was found to increase with increasing temperature in
reactors 1 and 4, but to decrease with increasing temperature
in the control case (reactor 3). The COD/N ratio had a strong
influence on nitrate removal. It was found that if the COD/N
ratio was <1.2, the nitrate removal efficiency was 85%. On the
other hand, if the ratio was >3, the removal was only 30%.
High concentrations of organics can promote rapid growth of
heterotrophic bacteria in the system, which, in turn, consumes
the organic carbon. This may affect the activity of autotrophic
bacteria, ultimately hampering the nitrate removal.

Espino-Valdés *et al.* (2003) conducted experiments to re-
move nitrogen species from wastewater by a reactor-based
biological process. Their system was an UF bioreactor fol-
lowed by a clarifier. This reactor was used as a nitrification
chamber and the air required was supplied from the bottom of
the reactor. The first clarifier was connected with a second UF
bioreactor followed by another clarifier. The UF bioreactor
was used as a denitrification chamber and methanol was
supplied from the bottom of the reactor. They used sand to
support the growth of biomass and the reactor was inoculated
with secondary sludge. About 81.3% of ammonia-nitrogen
was removed at 26.6°C and 94.8% at 32.2°C in 2.7 and 17.4 h,
respectively. The final concentration was 1.20 mg/L. Nitrate
and nitrite removal were also very significant in the reactor.
Nitrate + nitrite removal of about 85.6% at 28.7°C and 95.3%
at 33.3°C was observed in 2 and 4 h, respectively. The final
concentration was 1.6 mg/L. Nitrification and denitrification
biomass concentrations were 365 mg volatile suspended soil
(VSS)/L and 1,461 mg VSS/L. Both the effluent ammonia and
nitrate concentration were within the range acceptable in
Mexico. The aquifer recharge standard limits for ammonia and
nitrate-nitrogen are 5 and 10 mg/L, respectively, in Mexico.

Gálvez *et al.* (2003) tried using a submerged fixed film re-
actor to remove nitrogen from urban wastewater. There were
two columns in the system. The first column was a down-flow
nitrification reactor running under aerobic conditions and the
second one was an UF anoxic denitrification reactor. Air was
added in the first column and methanol was added in the
second one, both from the bottom. The reactor was filled with
clay schists from recycled construction materials and the
study emphasized the influence of hydraulic loading and
the air flow rate on nitrogen removal. The authors found
that low methanol concentrations reduced the nitrate re-
moval efficiency and there was a good correlation between
nitrogen removal and methanol concentration. The amount of
nitrification can be reduced by direct competition between
heterotrophic and autotrophic bacteria for substrate. The
nitrification in the system can be enhanced by decreasing the
organic loadings. The researchers concluded that the system
could achieve about 95% denitrification and about 75% COD
was removed (Gálvez *et al.*, 2003). When the denitrifiers were
given less methanol to consume over time, the nitrate removal
decreased but, again, high organic loading can hamper the
nitrogen removal process in the system.

Rodgers and Zhan (2004) used a vertically moving biofilm
system to remove nitrogen species from wastewater by bio-
logical processes. This small biological nutrient reduction
process was operated at 11°C and consisted of six polypro-
pylene tanks (with dimensions of $0.40 \times 0.40 \times 0.60$ m) in series,
six biofilm modules (one for each tank, with a specific surface
area of 6.48 m^2), a wastewater feed mixing tank, three peri-
staltic pumps (one for the feed mixing tank, one for tap water,
and the third for recirculation of nitrified wastewater), and a
pneumatic system complete with limit switches and delay
controllers. The delay controllers could lift and lower the
biofilm modules. The module speed was 0.2 m/s and the re-
circulation ratio was about 2.54. The first two tanks were
anoxic for denitrification and filled with cubes of corrugated
PVC sheets with a surface area of 150 m^2/m^3, and the other
four tanks were aerobic for nitrification, with a surface area of
media of 240 m^2/m^3. The flow rate was about 0.397 m^3/day.
The researchers found an overall COD removal of 94% with
an initial concentration of 485 mg/L, TN removal of 82% with
75 mg/L initial concentration, and NO$_3$-N removal of 95%
with 9.2 mg/L initial concentration in the system, without any
clogging. The denitrification rate was about 120.8 g/m^3/day
and 6.5 g/m^3/day in tanks 1 and 2, respectively. They con-
cluded that nitrification might be inhibited by competition for
DO between nitrifiers and heterotrophs (Rodgers and Zhan,
2004). Module speed was a very critical issue in operating the
system. The modules had to be sufficiently slow so that they
have sufficient contact time with the liquid. If the modules are
too fast, the biofilm layers may be washed out.

Güngör and Ünlü (2005) conducted nitrate and nitrite re-
moval from wastewater in a laboratory column experiment
with three types of soil. They used sandy clay loam, loamy
sand, and sandy loam and found significant nitrate and nitrite
removal (>90%) in all three soils. This experiment was very
important for nitrate removal by soil. It proved that some soils
have an affinity for nitrate but that this will vary from one
kind of soil to another. Forbes *et al.* (2005) used lightweight
expanded shale and masonry sand for the removal of phos-
phorus from secondarily treated municipal effluent. The
system contained three cells filled with expanded shale and
three cells filled with masonry sand. They found that sand
was a poor candidate for retaining phosphorus and expanded
shale had greater removal efficiency because of its larger
surface area. The chemical composition (i.e., Fe + Al) and
excellent hydraulic efficiency of shale were also responsible
for the removal of phosphorus (Forbes *et al.*, 2005). Sand can
remove phosphorus by adsorption if it is rich in clay and silt
particles or rich in minerals. Both of these may have been
absent in the masonry sand tested. Namasivayam *et al.* (2005)
used oyster shell powder (OSP) to remove phosphorus from
wastewater at 24°C. They found that raw oyster shells had no
affinity for phosphorus, but about 45% of phosphorus in batch
mode and 85% of phosphorus in continuous mode was re-
moved by OSP. They concluded that phosphorus was re-
moved by sorption as amorphous calcium phosphate on the
OSP surface and then slowly transformed into the more stable
hydroxyapatite (Namasivayam *et al.*, 2005).

Sengupta and Ergas (2006) experimented to remove nitrate
from wastewater by using sulfur, marble chips, limestone,
and oyster shell. In one system there were sulfur, marble, and
limestone and the other system contained sulfur, marble, and
oyster shell. Their experiment revealed the significant poten-

tial of using those solids as sorption media. They found that oyster shell (almost 98% $CaCO_3$) could remove 80% nitrate, whereas limestone removed only 56% nitrate. The pH and alkalinity were higher for oyster shell relative to limestone and marble chips. Oyster shell was very efficient at reducing nitrite accumulation and DO did not inhibit denitrification when oyster shell was used as the filter media. It was proved that the system containing oyster shell was following the sulfur-oxidizing denitrification pathway. Sulfur-oxidizing microorganisms generally follow aerobic autotrophic denitrification. A first-order denitrification was observed (about 0.028/h) in this study. It can be concluded that oyster shell is much more effective than limestone or marble chips for removing nitrate through sulfur-oxidizing microorganisms. Oyster shell is also a good candidate for controlling pH, which is a limiting factor for denitrification (Sengupta and Ergas, 2006).

Arami et al. (2006) studied the adsorption of direct (i.e., DR80 and DR81) and acid (i.e., AB92 and AR14) dyes by soy meal hull (SMH) to simulate the nutrients. The surface area of SMH was 0.7623 m^2/g. In all cases, the higher the initial dye concentration, the lower was the dye adsorption. They observed that, with an initial concentration of 50 mg/L and a pH of 2, the removal efficiencies of DR80, DR81, AR14, and AB92 were 98%, 97%, 86%, and 98%, respectively, after 120 min. The maximum monolayer adsorption capacity was 178.57 mg/g for DR80, 120.48 mg/g for DR81, 114.94 mg/g for AB92, and 109.89 mg/g for AB14. The adsorption capacity of SMH increased when the pH decreased. SMH has various functional groups such as amines, hydroxyl, and carbonyl groups. At lower pH (i.e., 2), significantly high electrostatic attraction might exist between the positively charged surface of SMH and negatively charged dyes. At higher pH (i.e., 10), SMH adsorbed less dyes because of higher negative charge on SMH surface. It was found that at pH 10, significant electrostatic repulsion existed between SMH surface and dyes. They found that pH and dye removal were inversely related. It was concluded that electrostatic attraction and the organic properties and structure of dye molecules might influence the adsorption process (Arami et al., 2006).

Smith et al. (2008) experimented on passive (i.e., not depending on pumping and external aeration) nitrogen removal from septic tank wastewater in Florida. They used three filter systems with the same structure. Each system had two columns: one was vertical and filled with stage 1 media (i.e., saturated condition, aerobic), and the other one was horizontal and filled with stage 2 media (i.e., unsaturated condition, anoxic). The stage 1 media were clinoptilolite (has ion exchange properties), expanded clay (increases the retention time and has adsorption properties), or tire crumb (has adsorption properties) and stage 2 media were elemental sulfur (an electron donor medium for denitrifiers), crushed oyster shell (used as an alkalinity source), or utelite (expanded shale with anion exchange properties). In system 1, the vertical column (1A) was filled with clinoptilolite and the horizontal column (2A) was filled with 75% sulfur and 25% oyster shell. In system 2, the vertical column (1B) was filled with expanded clay and the horizontal one (2B) with 60% sulfur, 20% oyster shell, and 20% expanded shale. In the third system, the vertical column (1C) was filled with tire crumb and the horizontal one (2C) was filled with 45% sulfur, 15% oyster shell, and 40% expanded shale. The researchers found strong removal of

nitrogen species. TN removal was about 97.1% for 1A + 2A, 97.7% for 1B + 2B, and 33% for 1C + 2C. Total inorganic nitrogen (TIN) removal was about 99.8% for 1A + 2A, 98.1% for 1B + 2B, and 34.4% for 1C + 2C. TN removal was about 50.6% for 1A, 26.1% for 1B, and 13% for 1C. NH_3-N removal was about 99.9% for 1A, 99.9% for 1B, and 60.5% for 1C. The denitrification process in the system was also good, with the lowest denitrification rate in column 2C. They proposed two possible explanations for this result: (1) as the amount of sulfur was lowest in this column, there were not enough electron donors for denitrification, and (2) harmful leachates from the tire crumb may have been present in this column. The DO concentration was 7.21 mg/L on average in stage 1 columns and 0.34 mg/L on average in stage 2 columns (Smith et al., 2008). The above discussion summarizes the most recent development in this field. Table 4 details the general success of using sorption media to remove various pollutants, especially nutrients, from wastewater under the conditions shown.

Groundwater treatment by sorption media

Groundwater is the most expensive and difficult type of water body to treat. Most of the existing research has been done in shallow groundwater. The main problem in working with groundwater is that water may change its flow pathway during the test. Benson and Lee (2001) used waste foundry sand to treat groundwater. Table 5 summarizes the sorption media used to treat groundwater.

Schipper et al. (2005) performed an experiment with a sawdust denitrification wall to remove nitrate in shallow groundwater with an HRT of 5 days. They filled a trench (about 35 m long, 1.5 m deep, and 1.5 m wide) with Monterey pine sawdust (Pinus radiata D. Don; 30% by volume) mixed with the excavated soil. The authors suggested that the nitrate concentration was the limiting factor to denitrification, rather than carbon, because the denitrification rate increased when additional nitrate was added to the soil. Because of the higher nitrate level, the denitrifiers could grow easily and subsequently increased the denitrification rate. No nitrate accumulation was observed in the soil OM and nitrate was not transformed into ammonia. They found a nitrate-N removal rate of 1.4 g N/m^3 of wall per day, which was about 97.2% of nitrate removal (Schipper et al., 2005).

Landfill leachate treatment by sorption media

Groundwater can also be contaminated by landfill leachate. Some protective measures are taken during landfill construction, but the condition of the system may deteriorate with time and start to pollute the groundwater. For this reason, it is sometimes necessary to treat the landfill leachate. Table 6 summarizes the use of sorption media in the treatment of landfill leachate.

Jokela et al. (2002) conducted an experiment to eliminate nitrogen from municipal landfill leachate by a biological process. Nitrification was tested in three types of reactors: (1) UF nitrification filter with crushed brick as a filter medium, (2) down-flow nitrification filter with wood chips, and (3) nitrification in suspended carrier biofilm process (SCBP). All the nitrification reactors were inoculated by nitrifying activated sludge collected from a sewage treatment plant. In the UF

TABLE 4. NUTRIENT REMOVAL EFFICIENCY OF DIFFERENT SORPTION MEDIA IN WASTEWATER TREATMENT

No.	Sorption media	Mechanism	Removal efficiency	References
1	Tire chips	Biological process	VOC	Shin et al. (1999)
2	Polyurethane-based porous media	Nitrification/denitrification	100% ammonia and nitrite (initial concentration 50 mg/m³), ammonia-loading rate 1.8 kg NH_4-N/m³/day	Han et al. (2001)
3	Sulfur: limestone autotrophic denitrification	Denitrification/chemical reaction	90%–100% nitrate with alkalinity control and mixing, about 80%–85% nitrite without alkalinity control (initial concentration 30 mg N/L and loading rate 1 g NO_3-N/m³/day)	Zhang (2002)
4	Sand	Nitrification/denitrification	81.3% ammonia-nitrogen (initial concentration 22.4 mg N/L), 85.6% nitrate + nitrite (initial concentration 55 mg N/L)	Espino-Valdés et al. (2003)
5	Clay schists	Nitrification/denitrification	95% denitrification (initial concentration 80 mg N/L), 75% COD (initial concentration 450 mg N/L), nitrogen removal rate 0.64 kg N/m³/day, hydraulic loading rate 0.71 m³/m²/h, HRT 1.6 h	Gálvez et al. (2003)
6	Biofilm modules	Nitrification/denitrification	94% COD, 82% TN, 95% NO_3-N	Rodgers and Zhan (2004)
7	SCL	Nitrification/denitrification	90% nitrate + nitrite (initial concentration 11.87 mg N/L)	Güngör and Ünlü (2005)
	LS		90% nitrate + nitrite (initial concentration 11.87 mg N/L)	
	SL		90% nitrate + nitrite (initial concentration 11.87 mg N/L)	
8	Lightweight expanded shale Masonry sand	Nitrification/denitrification		Forbes et al. (2005)
9	OSP	Adsorption	45% phosphorus in batch mode, 85% phosphorus in continuous mode (initial concentration 10 mg/m³)	Namasivayam et al. (2005)
10	Marble chips Limestone Oyster shell	Adsorption	Only nominal amount 56% of nitrate (initial concentration 40 mg N/L) 80% nitrate (initial concentration 40 mg N/L)	Sengupta and Ergas (2006)
11	Soy meal hull	Adsorption	98% DR80, 97% DR81, 86% AR14, 98% AB92 (initial concentration 50 mg/L)	Arami et al. (2006)
12	Clinoptilolite	Nitrification/denitrification	50.6% TN (initial concentration 77.4 mg/L, for all cases), 99.9% ammonia (initial concentration 52.5 mg/L, for all cases)	Smith et al. (2008)
	Expanded clay		26.1% TN, 99.9% ammonia	
	Tire crumb		13% TN, 60.5% ammonia	
	Clinoptilolite + (75% sulfur + 25% oyster shell)		97.1% TN, 99.8% TIN (initial concentration 56.8 mg/L), hydraulic loading rate 110.42 L/m²/day	
	Expanded clay + (60% sulfur + 20% oyster shell + 20% expanded shale)		97.7% TN, 98.1% TIN, hydraulic loading rate 120.2 L/m²/day	
	Tire crumb + (45% sulfur + 15% oyster shell + 40% expanded shale)		33.% TN, 34.4% TIN, hydraulic loading rate 102.27 L/m²/day	

COD, chemical oxygen demand; TIN, total inorganic nitrogen; VOC, volatile organic carbon.

TABLE 5. SORPTION MEDIA USED TO TREAT GROUNDWATER

No.	Sorption media	Additional environmental benefits	Physical/chemical properties	References
1	Waste foundry sand	TCE, Zn, metolachlor, alachlor, herbicides		Benson and Lee (2001)
2	Sawdust	Monterey pine (*Pinus radiata* D. Don) sawdust	97.2% nitrate (initial concentration 50 mg N/L), nitrate-N removal rate 1.4 g N/m³/day	Schipper *et al.* (2005)

TCE, trichloroethylene.

filter, nitrification efficiency was about 60%–88% in 60 days, and after 60 days it was above 90%. COD removal efficiency ranged from 26% to 62%. In the down-flow filter, the nitrification efficiency was about 90% after 70 days and no COD removal was detected. With SCBP, the nitrification efficiency was 75%–99% between 112 and 196 days and COD removal was 53%–63%. They suggested that the UF nitrification mode was more efficient because of its higher HRT. Denitrification was tested in a landfill waste column fed by a nitrified sample from the SCBP. It was concluded that leachates with high COD might inhibit denitrification by favoring the growth of heterotrophs over nitrifiers (Jokela *et al.*, 2002).

Lisi *et al.* (2004) tested the use of granulated tires for the removal of nitrate. They found that 48 kg of tire crumb can remove 16.2 g of NO₃-N by adsorption (Lisi *et al.*, 2004). Savage and Tyrrel (2005) used wood mulch, compost, soil, broken brick, and polystyrene packaging to remove NH₃-N and biochemical oxygen demand (BOD₅) from compost leachate. They concluded that wood mulch (75% removal) and compost (55% removal) had better removal efficiencies, and polystyrene (31% removal) was the least effective at removing NH₃-N. Similarly, for BOD₅, compost had a better removal efficiency (i.e., about 78%) and polystyrene was the least efficient (i.e., about 34%). The researchers found that compost and wood mulch had a tendency to increase the pH and concluded that specific surface area, void space, permeability, media durability and strength, and absorption/adsorption capacity might influence removal efficiency (Savage and Tyrrel, 2005).

Kietlińska and Renman (2005) applied sand, BFS, and Polonite® (a calcinated Opoka—a siliceous sedimentary rock) to remove nitrogen species and heavy metals from landfill leachate in a column study. Peat was mixed with each of them

in a ratio of 1:4 by volume. Total inorganic nitrogen could be removed by sand (about 4%), Polonite (18%), and BFS (8%). Kietlińska and Renman inferred that the wollastonite in Polonite might be responsible for the removal of nitrogen species, as wollastonite has some preference for nitrogen species, especially ammonia. Polonite could also remove 89% Mg, 99% manganese, 93% Fe, 86% Zn, 86% zirconium (Zr), 85% barium (Ba), 67% Cu, 77% titanium (Ti), 60% yttrium (Y), and 30% cobalt (Co); BFS could remove 20% Fe, 62% Zn, 63% Zr, 31% Ba, 66% Cu, 33% Co, 19% Ni, and 16% molybdenum (Mo); and sand could remove 25% Cu and 15% Mo. Polonite might be removing the metals by precipitation, ion exchange, and adsorption. They concluded that pH can affect the removal of heavy metals by Polonite, and hydroxide precipitation is responsible for the high removal of metals by forming insoluble precipitates. Table 7 shows the general success of using sorption media to remove various pollutants, especially nutrients, in landfill leachate under the given conditions.

Drinking water treatment by sorption media

Applications of biological processes to drinking water treatment are common nowadays, although there is a danger on unintentional introduction of bacterial contaminants. Disinfectant should be used to reduce possible bacterial contamination. However, nutrients and heavy metals can be removed by adsorption and ion exchange processes with sorption media. For drinking water generation, the use of sorption media is much more attractive than biological processes. As sorption media are good supports for bacterial growth, they should be changed frequently when treating drinking water. Table 8 lists the sorption media that have been applied to drinking water treatment.

TABLE 6. SORPTION MEDIA USED TO TREAT LANDFILL LEACHATE

No.	Sorption media	Additional environmental benefits	Physical/chemical properties	References
1	Wood chips compost with household waste Crushed bricks			Jokela *et al.* (2002)
2	Tire crumb	VOC		Lisi *et al.* (2004)
3	Wood chips Oversized pulverized brick Polystyrene packing			Savage and Tyrrel (2005)
4	Peat Polonite	Zn, Ni, Co, Ti, Cu, Ba	Manufactured from a cretaceous rock Opoka (SiO₂ 39.4%, CaO 42%, Al₂O₃ 4.3%, Fe₂O₃ 2%)	Kietlińska and Renman (2005)
	Blast furnace slag		SiO₂ 36.2%, CaO 35%, MgO 13.4%, Al₂O₃ 10.6%	

TABLE 7. NUTRIENT REMOVAL EFFICIENCY OF DIFFERENT SORPTION MEDIA IN LANDFILL LEACHATE TREATMENT

No.	Sorption media	Mechanism	Removal efficiency	References
1	Up-flow nitrification filter with crushed brick as a filter medium	Nitrification/ denitrification	Nitrification efficiency was about 60%–88% in 60 days, and after 60 days it was above 90%, COD removal efficiency ranged from 26% to 62% (initial concentration 60–170 mg N/L and 230–510 mg O_2/L, for all cases)	Jokela et al. (2002)
	Down-flow nitrification filter with wood chips		Nitrification efficiency was about 90%	
	Nitrification in suspended carrier biofilm process		Nitrification efficiency was 75%–99%, COD removal was 53%–63%	
2	Tire crumb	Adsorption	48,000 g of tire crumb can remove 16.2 g of NO_3-N	Lisi et al. (2004)
3	Wood mulch	Adsorption/ nitrification/ denitrification	75% NH_3-N (initial concentration 705 mg/L, for all cases), 70% BOD_5 (initial concentration 48,720 mg/L, for all cases)	Savage and Tyrrel (2005)
	Compost		55% NH_3-N, 78% BOD_5	
	Soil		38% NH_3-N, 44% BOD_5	
	Broken brick		35% NH_3-N, 74% BOD_5	
	Polystyrene		31% NH_3-N, 34% BOD_5	
4	Sand + peat	Precipitation, ion exchange, adsorption	2% Mg (initial concentration 101 mg/L, for all cases), 2% S (initial concentration 124 mg/L, for all cases), 25% Cu (initial concentration 0.03 mg/L, for all cases), 15% Mo (initial concentration 0.02 mg/L, for all cases), 4% TIN (initial concentration 105.9 mg/L, for all cases)	Kietlińska and Renman (2005)
	Blast furnace slag + peat		89% Mg, 4% S, 99% Mn (initial concentration 0.57 mg/L, for all cases), 93% Fe (initial concentration 0.61 mg/L, for all cases), 86% Zn (initial concentration 0.08 mg/L, for all cases), 86% Zr (initial concentration 0.003 mg/L, for all cases), 85% Ba (initial concentration 0.19 mg/L, for all cases), 67% Cu, 77% Ti (initial concentration 0.002 mg/L, for all cases), 60% Y (initial concentration 0.001 mg/L, for all cases), 30% Co (initial concentration 0.004 mg/L, for all cases), 2% Ni (initial concentration 0.02 mg/L, for all cases), 8% tin	
	Polonite + peat		20% Fe, 62% Zn, 63% Zr, 31% Ba, 66% Cu, 33% Co, 19% Ni, 16% Mo, 18% tin	

BOD, biochemical oxygen demand.

TABLE 8. SORPTION MEDIA USED BY DIFFERENT RESEARCHERS TO TREAT DRINKING WATER

No.	Sorption media	Physical/chemical properties	References
1	Newspaper	0.40-cm-width ribbons (25.49% extractives, 43.11% cellulose, 29.59% lignin, 2.59% ash)	Volokita et al. (1996)
2	Sulfur	$D = 2.38$–4.76 mm	Darbi et al. (2002); Darbi et al. (2003)
	Limestone	$D = 2.38$–4.76 mm	
3	Cotton waste		Rocca et al. (2005)

TABLE 9. NUTRIENT REMOVAL EFFICIENCY OF DIFFERENT SORPTION MEDIA IN DRINKING WATER TREATMENT

| No.	Sorption media	Mechanism	Removal efficiency	References
1	Shredded newspaper	Denitrification	77.78% of nitrate after 30 days and 38.9% of nitrate after 120 days (initial concentration 22.58 mg N/L), nitrogen removal rate 0.73 mg N/g paper/day	Volokita et al. (1996)
2	Sulfur + limestone (1:1)	Denitrification	98% nitrate (initial concentration 27 mg N/L)	Darbi et al. (2002)
3	Cotton	Denitrification	91.5% nitrate (initial concentration 100 mg N/L)	Rocca et al. (2005)
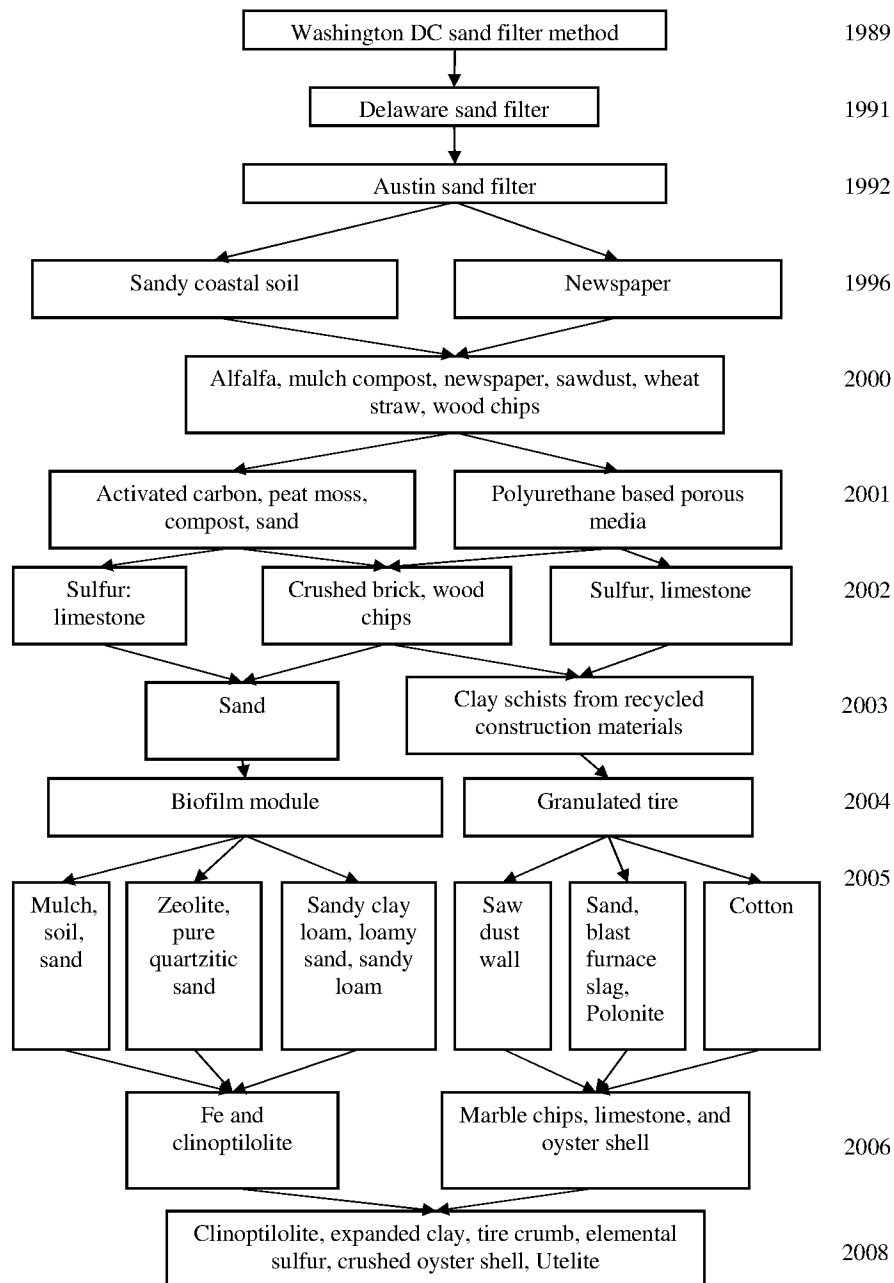
FIG. 1. Flow chart showing the methods of nitrogen species removal in chronological order of first application.
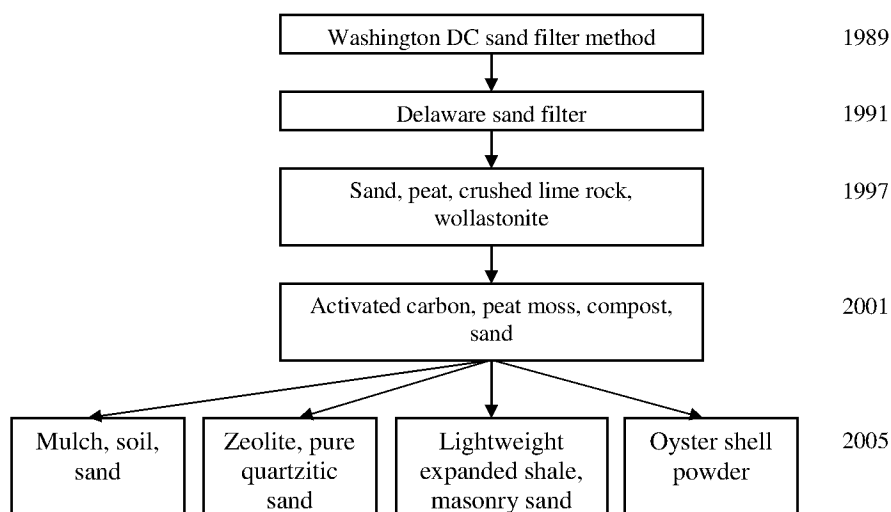
FIG. 2. Flow chart showing methods of phosphorus species removal in chronological order of first application.

Volokita *et al.* (1996) used shredded newspaper for denitrification of drinking water in a column study. Newspaper is a good source of carbon and colony support for microbial populations. These authors found that the system could remove about 77.78% of the nitrate after 30 days and 38.9% after 120 days. This longer time was necessary to accommodate the growth of sufficient denitrifying bacteria in the system. The study showed that temperature and retention time have a marked effect on cellulose-based denitrification. The retention time can be increased by decreasing the flow or by increasing the length of the system. The ink on newspaper also affected microbial growth in the system, but was not a limiting factor. It was observed that the highest denitrification rate occurred at temperatures of 25°C–32°C and with unprinted newspaper (Volokita *et al.*, 1996).

Darbi *et al.* (2002) assessed sulfur and limestone for nitrate removal through autotrophic denitrification from potable water in a batch study. In this experiment, sulfur was used as an electron donor and limestone was used to maintain the pH. The optimum mixing ratio of sulfur and limestone was 1:1, yielding about 98% nitrate removal and minimizing sulfate production at pH 7. Sulfate production was also decreased when the nitrate removal was increased. The authors suggested that increasing the retention time might result in higher removal efficiency (Darbi *et al.*, 2002). The same researchers conducted a column test for nitrate removal from potable water (Darbi *et al.*, 2003). In this study, there were three UF columns filled with elemental sulfur and limestone at ratios of 1:1, 2:1, and 3:1. All the columns were inoculated with *Thiobacillus denitrificans*. With 26 h HRT, the nitrate removal was about 95%–100% and nitrite concentrations were below 1 mg NO_2-N/L in all columns. The nitrate removal and sulfate production were highest when the sulfur-to-limestone ratio was 2:1. It was noticed that sulfate (SO_4^{2-}) production increased with increase of both volumetric loading rate and nitrate removal. About 6 mg SO_4^{2-} was produced for 1 mg NO_3-N removal (Darbi *et al.*, 2003).

Rocca *et al.* (2005) used cotton-supported heterotrophic denitrification (HD) for the removal of nitrate from drinking water. There were two reactors: an HD reactor followed by a trickling sand filter. Cotton (the purest form of naturally occurring cellulose) was used as the organic carbon source and

supporting material for the growth of denitrifiers. Nitrate removal was about 91.5% at a system temperature of 28°C. Nitrate removal decreased with increasing temperature and increased with increasing water velocity (Rocca *et al.*, 2005). Table 9 integrates the general success of using sorption media to remove various pollutants, especially nutrients, in the drinking water under some given conditions.

Figures 1 and 2 illustrate the timeline of how using sorption media for nutrient removal has progressed over the past 3 decades. The most intensive work was performed in recent years. This was triggered by the acute need of a regulatory framework for nutrient control in on-site wastewater treatment, stormwater treatment, combined sewer overflow, and LID.

Conclusions

This article describes the most important research for nutrient removal via sorption media mixtures for stormwater reuse, wastewater treatment, landfill leachate treatment, groundwater remediation, and drinking water treatment. Media mixtures can provide a good organic carbon source if sawdust/compost is included. They can create excellent environments for the growth of microorganisms that foster both nitrification and denitrification at the laboratory scale. Field applications focusing on the practical scale-up of nutrient removal technologies, however, remain of critical concern. Cost-effectiveness assessment for nutrient removal will be as important as the consideration of sustainable development. The companion paper will address the field applications by a more elaborate way to clarify some of the application challenges, perspectives, and potentials.

Author Disclosure Statement

No competing financial interests exist. The authors are grateful for all the data and reports cited and used in this study. Conclusions and opinions presented in this paper are those of the authors, and do not necessarily represent the position of any funding agency. Mention of commercial products, trade names or services in the paper does not convey endorsement, or recommendation.

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Appendix: Nutrient Forms Involved in This Study

(1) Nitrogen species

- Total nitrogen (TN) = organic N + ammonia N + nitrate N + nitrite N
- Total Kjeldahl nitrogen (TKN) = organic N + ammonia N
- Organic nitrogen = Filtrable organic N + nonfiltrable organic N
- Total inorganic nitrogen (TIN) = ammonia N + nitrate N + nitrite N
- Total oxidized nitrogen (TON) = nitrate N + nitrite N
- TN = TKN + TON

(2) Phosphorus species

- IP = inorganic phosphate
- OP = orthophosphate
- CP = condensed phosphates (also known as metaphosphates or polyphosphates)
- IP = OP + CP
- SP = soluble phosphorus
- SRP = soluble reactive phosphorus ($\sim$ soluble inorganic orthophosphate (PO_4))
- SUP = soluble unreactive phosphorus (= SP – SRP)
- SOP = soluble organic phosphorus
- PP = particulate phosphorus
- TP = total phosphorus
- TP = SRP + SUP + PP